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TITLE TIME-RESOLVED REFLECTIVITY STUDY OF LASER-EXCITED LAYERED COMPOUNDS

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TIME-RESOLVED PICOSECOND REFLECTIVITY STUDY OF LASER-EXCITED LAYERED COMPOUNDS

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ABSTRACT

We have employed the pump-and-probe technique to perform picosecond time resolved measurements of the reflectivity changes in two archetypal layered compounds, 1T-TiS₂ and 1T-TiSe₂ probed at 1.064 μm after pumping by 20 ps, .532 μm laser pulses. At the threshold fluence, $\sim 40 \text{ mJ/cm}^2$, the reflectivity drops sharply, marking the occurrence of a phase transformation on the surface of the sample. Above threshold, the reflectivity reaches a value as low as ~ 0.1 at high fluences, strongly suggesting that, like in graphite, the high temperature phase is not metallic.

INTRODUCTION

Very recently, the transient optical properties of crystalline graphite surfaces excited by visible picosecond laser pulses have been investigated with 20 - 30 ps time resolution ^{1,2}. Reflectivity measurements at low excitation levels have revealed the presence of a fast decaying electron-hole plasma evolving from the initial semimetallic configuration. More interestingly, at a well defined pump threshold value of $\sim 140 \text{ mJ/cm}^2$ a phase transition occurs, which is characterized by lower reflectivity values. We have concluded that the high temperature phase is not metallic, having a lower value of the index of refraction, but, rather, intermediate between the one of graphite and that of diamond. This unexpected new phase is presumably caused by a strong perturbation of the spatial arrangement of carbon atoms in the graphite lattice, which consists of hexagonally arranged, loosely stacked atomic layers. The question thus arises whether the electronic properties of the high temperature phase originate from a particular initial structure. For this reason, it is of interest to investigate other archetypal layered compounds.

In this paper, we have chosen two crystalline layered compounds, 1T-TiS₂ and 1T-TiSe₂. The titanium atoms are octahedrally coordinated with chalcogen atoms forming a chalcogen-metal-chalcogen sandwich layer configuration.³ In a plane, atoms are hexagonally packed. However, the coordination around the non-metal is quite lopsided, leading to the marked cleavage properties perpendicular to the hexagonal symmetry axis. The basic atomic structure of loosely coupled X - Ti - X (X = S, Se) atom sheet sandwiches makes the mechanical, thermal and electrical properties extremely anisotropic, like those of graphite. The lattice constants for TiS₂⁴ are slightly smaller

than those of TiSe_2 .⁵ It is now well established that the former is an extrinsic semiconductor with an indirect band gap of 0.2 - 0.3 eV,⁶⁻⁹ but it is normally non-stoichiometric and thus exhibits metallic conductivity arising from an excess of Ti atoms. TiSe_2 is an intrinsic semimetal.¹⁰⁻¹² All these physical properties are similar to those of graphite. Hence, it is of importance to perform experiments on the high temperature regime for these compounds and then compare the results with those of highly oriented pyrolytic graphite (HOPG).^{1,2}

EXPERIMENTAL RESULTS

We have performed a series of time-resolved picosecond pump-and-probe measurements similar to those made on HOPG.^{1,2} The pumping was provided by 20 ps pulses at 0.532 μm by frequency doubling the output of an active-passive mode-locked Nd-YAG laser system. The variable time delayed 1.064 μm pulses

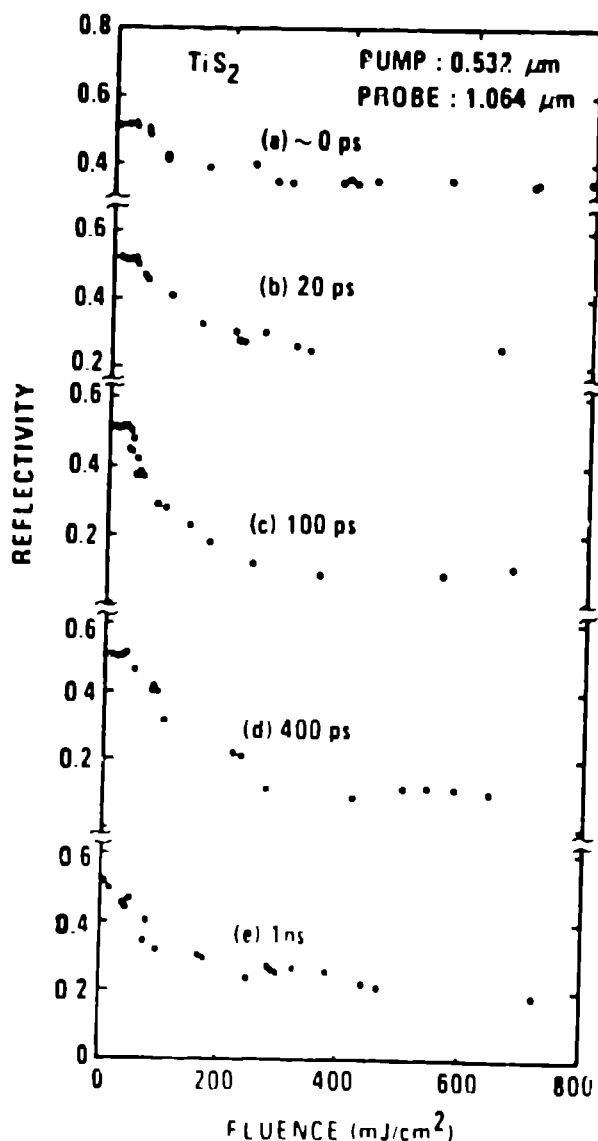


Figure 1. Reflectivity of 1T- TiS_2 at 1.064 μm as a function of 0.532 μm pump fluence at the delay times shown.

were used to monitor the reflectivity at the center of the excited surface. Near normal incidence angles are employed for both pump and probe laser beams. All the samples used in this work were single crystals.

We have found that a damage spot appears on the sample above a fixed green pump fluence value. Our optical micrographs show the appearance of a black ring marking the damage area. Its formation suggests the occurrence of a phase transformation. The size of the ring strictly follows the spatial variations of the gaussian fluence distribution of the laser beam, indicating the thermal origin of the effect. The extrapolated value of the threshold fluence is $F_{th} = 43 \text{ mJ/cm}^2$.

Figure 1 shows our reflectivity results obtained on 1T-TiS₂ single crystal probed at $1.064 \mu\text{m}$ as a function of the $0.532 \mu\text{m}$ pumping fluence at the different delay times t_d . As Figure 1 (a - d) shows, the reflectivity drops sharply around 40 mJ/cm^2 for all positive delay times t_d , in agreement with the value of F_{th} obtained from the post-experimental examination of the damaged area discussed above. Consequently, like in HOPG, we may identify F_{th} as the threshold fluence for an ultrafast phase transition. The drop is particularly pronounced at $\sim 100 \text{ ps}$, where the reflectivity reaches a value as low as ~ 0.1 from the initial value of 0.52 . This variation exceeds the similar variation in the reflectivity observed in HOPG at the same wavelength. It has been shown that for a delay time of $\sim 10 \text{ ps}$, only one atomic layer can escape the surface of the sample,¹³ giving a negligible contribution to the reflectivity. As shown in Fig. 1-(a), even when the probe pulse overlaps the pump pulse ($t_d \sim 0 \text{ ps}$) the reflectivity drops above the threshold fluence value, thus clearly demonstrating that the decrease of the reflectivity is not due to evaporation.

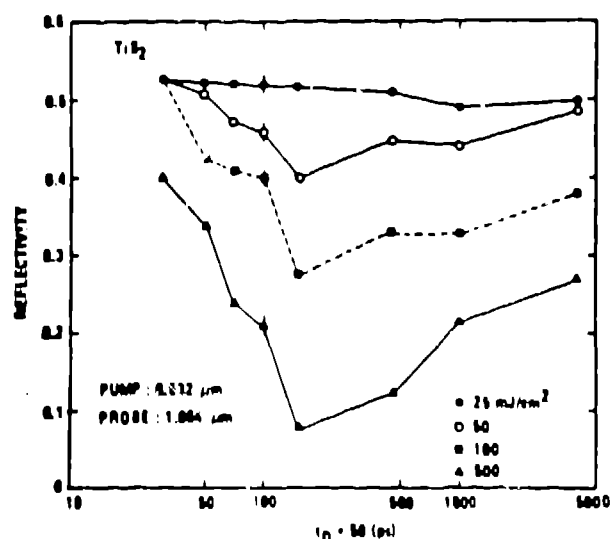


Figure 2. Reflectivity of 1T-TiS₂ at $1.064 \mu\text{m}$ as a function of probe delay time t_d , for various pump fluences. The origin of t_d is shifted by 50 ps .

In Figure 2 we plot the measured reflectivity as a function of the delay time, t_d . Note that the time origin in the abscissa has been shifted by 50 ps in order to accommodate the data taken

before the arrival of the pump pulse. At 25 mJ/cm^2 , the reflectivity is practically time independent. At fluences greater than F_{th} , the reflectivity values are decreasing at first, reaching a minimum at $\approx 200 \text{ ps}$, and then recover to higher levels. This behavior of the reflectivity clearly indicates the occurrence of a transient new phase induced by the pump laser pulse and presumably terminated by heat dissipation in the bulk of the crystal. The lack of data on the thermal properties of these compounds prevents quantitative estimates. The final value $R_{\infty} = .35$ of the reflectivity taken at very long delay times is lower than the initial one, indicating the presence of a permanent damage on the surface as soon as the threshold fluence value F_{th} is exceeded.

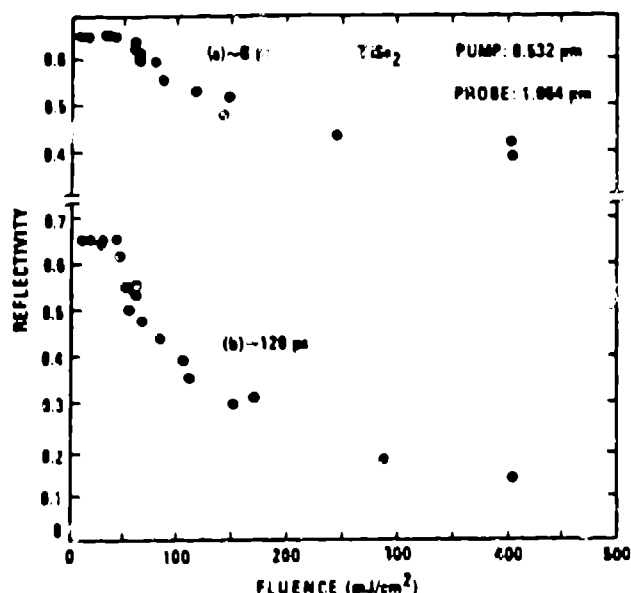


Figure 3. Reflectivity of $1T\text{-TiSe}_2$ at $1.064 \mu\text{m}$ as a function of $0.532 \mu\text{m}$ pump fluence at the delay (a) - 0 ps and (b) - 120 ps .

The reflectivity data for the semimetal $1T\text{-TiSe}_2$, illustrated in Figure 3, are qualitatively similar to those for the semiconductor $1T\text{-TiS}_2$. Also, the temporal behavior at the different fluences appears similar to the one presented in Fig 2. Our results indicate that the high temperature optical behavior of these two materials is independent of the initial electronic properties of these two layered compounds.

CONCLUSIONS

The transient optical properties of TiS_2 and TiSe_2 crystals under picosecond visible excitation have been investigated at $1.064 \mu\text{m}$ with picosecond time resolution. Below the threshold fluence of $\approx 40 \text{ mJ/cm}^2$ for 20 ps , $0.532 \mu\text{m}$ pump laser pulses, no significant changes in the reflectivity at $1.064 \mu\text{m}$ for both materials have been observed. Due to the small value of the band gap in TiS_2 as compared to the probing photon energy, the plasma contribution to the dielectric constant appears to be negligible. Presumably, longer wavelengths and/or larger incidence angles have to be used to detect plasma effects from the optical response of these materials.

At fluences exceeding the threshold value F_{th} the reflectivity decreases to values as low as ≈ 0.1 . These reflectivity changes occur during the exciting laser pulse. This suggests that the high temperature phase of these compounds is not metallic. The laser pump pulse gives rise to a transition from a semimetallic or small-band-gap semiconducting electronic structure into a rather transparent phase, where a smaller number of carriers interacts with the incoming laser pulse. Light can therefore travel into the material for distances exceeding the original extinction depth. Comparison ¹⁴ of the morphology of picosecond with nanosecond laser irradiated graphite indicate that ultrafast melting occurs at fluences exceeding F_{th} . Similar considerations apply here for $TiSe_2$ and TiS_2 , the critical value for melting being lower due to the different optical and thermal properties of these compounds.

This comparative study suggests that a similar, non-metallic high temperature phase exists for archetypal layered structures other than graphite. The electronic properties at high temperatures could originate from the initial presence of a layered structure which undergoes heavy disruption under laser excitation. A deeper insight, however, is necessary to unravel the true nature of the structure. The transient optical properties, as derived i.e. by pump-and-probe experiments or time-resolved ellipsometry at different wavelengths, can provide useful information if coupled with other firm optical and thermal data on the materials under study.

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